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Modelling of thorium extraction by TBP

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Abstract

This study focuses on thorium extraction modelling by a 30%$_{vol}$ TBP in TPH diluent, to simulate the behaviour of this actinide in extraction cycles. Experimental batch studies were performed to complete the set of distribution data on thorium and 30%TBP available in the literature. A thorium extraction model was developed and implemented in the PAREX process simulation code. Simulation results are confronted to available distribution data as well as feed back data from industrial plant.

Keywords: Th; U; solvent extraction; modelling

1. Introduction

TBP is an organophosphorus extractant used in nuclear industry to recover and purify uranium (U) and plutonium (Pu) by solvent extraction from mining concentrates or spent fuels dissolved in nitric acid (HNO_3). Among impurities, thorium (Th) should be considered since it is continuously produced by radioactive decay of ^{238}U or ^{232}U found in ore or reprocessed fuels. Thorium is extracted by TBP but with distribution ratio lower than U(VI). Thus, in an uranium purification cycle using TBP as solvent, Thorium tends to accumulate in extraction section just behind the uranium front (cf.Fig 4). This study focuses on thorium extraction modelling by a 30%vol TBP in TPH diluent, to simulate the behaviour of this actinide in extraction cycles, in the PUREX process. The

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Th(IV) distribution ratios measured are presented as well as the Th(IV) extraction model developed and implemented in the PAREX code.

Nomenclature

T	temperature	γ	activity coefficient
[C]aq	aqueous concentration	psk	pseudo constant
[C]org	organic concentration	D	distribution ratio
K	thermodynamic equilibrium constant	M	mol/L

2. Experimental work

Data published by Germain [1], give distribution data of thorium at different aqueous nitric acid concentration (1M to 4M) and organic uranium concentrations (0 g/L to 100 g/L). Thorium concentration in the aqueous phase is about 200 mg/L. This set of data is well adapted to our modelling concern. Therefore we decided to complete this set of data with thorium distribution ratio at lower nitric acid concentration (0.5M) and also at 1M for comparison with the distribution data of Germain. In our work the thorium concentrations were similar to those used by Germain. In addition, for series of data at 1M nitric acid, trace amount of thorium was used (~5 ng/L).

Th(IV) distribution ratios with 30%TBP/TPH were acquired at different thorium and nitric acid concentrations with and without uranium loading. After phase separation, thorium concentration was determined in both phases by three different analytical techniques (ICP-AES, X-ray fluorescence and γ spectrometry by measuring ^{234}Th coming from ^{238}U) in order to confirm the results. In ICP experiments, thorium concentration in organic phase was measured after stripping quantitatively thorium in ammonium carbonate at 50°C. As shown in figure 1, distribution ratios measured by the different techniques are in close agreement.

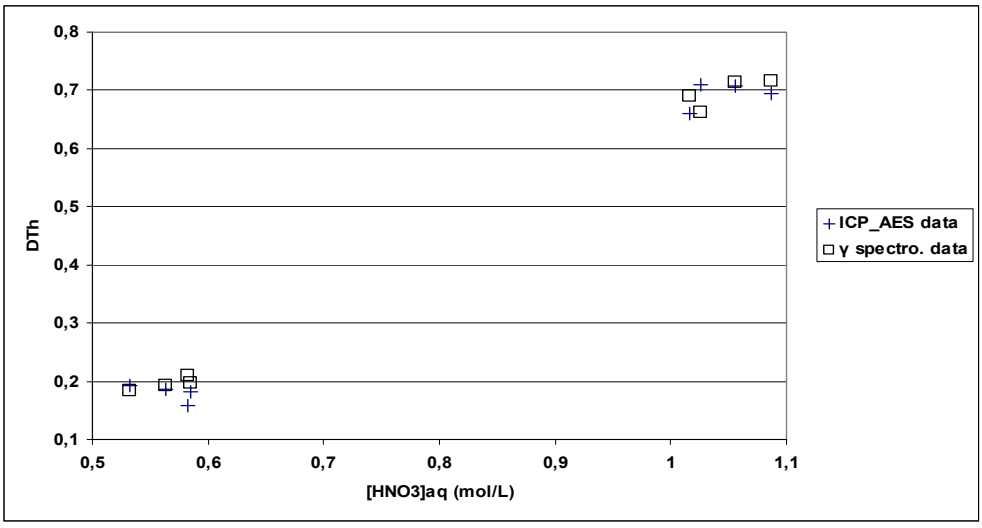

Fig.1. Comparison between results obtained by ICP-AES and γ spectrometry.

3. The thorium extraction model

3.1. Extraction model

Extraction equilibrium of Th(IV) by TBP with nitrate ion is:

$$Th_{aq}^{4+} + 4NO_{3aq}^{-} + nTBP_{org} \leftrightarrow (Th(NO_3)_4, nTBP)_{org} \quad \textit{with n=2 or 3}$$

For this equilibrium, the mass action law takes the form:

$$K_{Th(iv)} = \frac{[Th(NO_3)_4, nTBP]_{org}}{[Th^{4+}]_{aq}[NO_3^-]_{aq}^4[TBP]_{org}^n} \cdot \frac{\gamma_{Th(iv)org}}{\gamma_{Th(iv)\ aq} \cdot \gamma_{NO_3aq}^4 \cdot \gamma_{TBPorg}^n}$$

To compute the distribution ratios, as a function of species concentrations, the equilibrium constant must thus be determined, along with the activity coefficients for the various species, in the aqueous and organic phases. An approach of the semi-empirical type was chosen, to determine these distribution ratios. This approach is based on the observation that activity coefficients, in the aqueous phase, are chiefly dependent on nitrate molality, while those relating to the organic phase show little variation, in the region considered (the organic phase is taken as an ideal solution). So, the organic and aqueous concentration can be linked by a pseudo constant which is a function of the nitrate concentration and temperature:

$$psk_n = \frac{K_{Th_n}[NO_3^-]_{aq}^4}{\pi_i \gamma_i^{pi}} = \frac{[Th(NO_3)_4, nTBP]_{org}}{[Th^{4+}]_{aq}[TBP]_{org}^n}$$

Parameters of pseudo-constants are adjusted thanks to an optimization method, coupled with the model using Scilab©, which minimized the root mean square deviation (RMSD) between computed organics concentrations by the model and experimental organic concentrations. Agreement between computed and experimental data is defined by RMS and mean deviation (MD).

The experimental data used for the model optimization are extracted from the experimental work and from Germain publication [1]. Furthermore, only data of thorium extraction carried out around 22 °C with TBP 30% in nitric acid were considered.

Optimization was carried out considering that two thorium complexes extracted by TBP, $Th(NO_3)_4TBP_n$ (n=2 and 3).

3.2. Confrontation of the extraction model to available distribution data

Figures 2 and 3 show the comparison between computed and experimental Th(IV) distribution ratios. Considering all the data used for the optimization, the MD is -7% and RMSD is 25.5%. The measurements are quite dispersed. For data at 1M nitric acid, data obtained with trace amount of thorium (1-5 ng/l) are different from those obtained with higher concentration of thorium (200 mg/L) (cf. Fig. 2). This could explain the great RMSD observed. Data obtained by Germain for 1M differ from data obtained in this work, and were not

considered in elaborating the extraction model. Data obtained by Germain at other acidities were taken into account.

Figure 3 shows that the agreement between measured and computed values is acceptable.

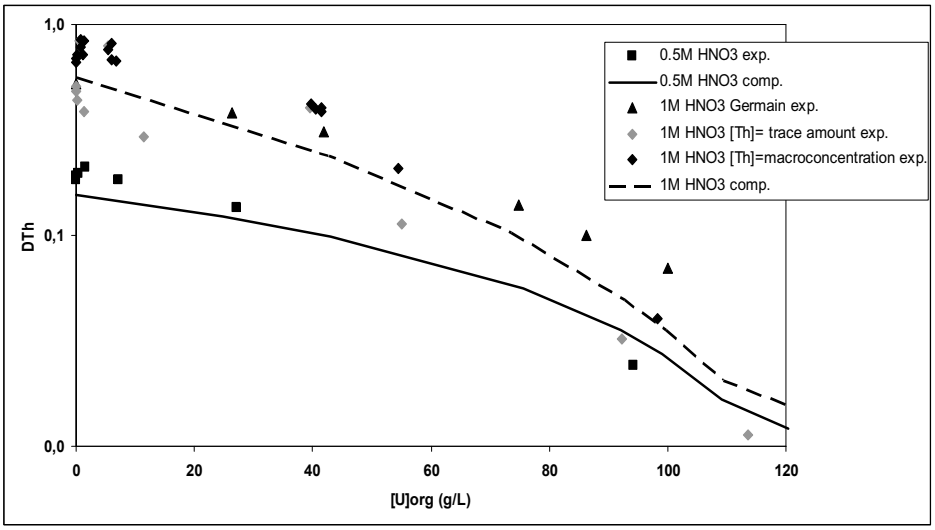

Fig.2. Comparison between computed and experimental Th(IV) distribution ratios used for the optimization of pseudo-constants for HNO3= 0.5 and 1 M.

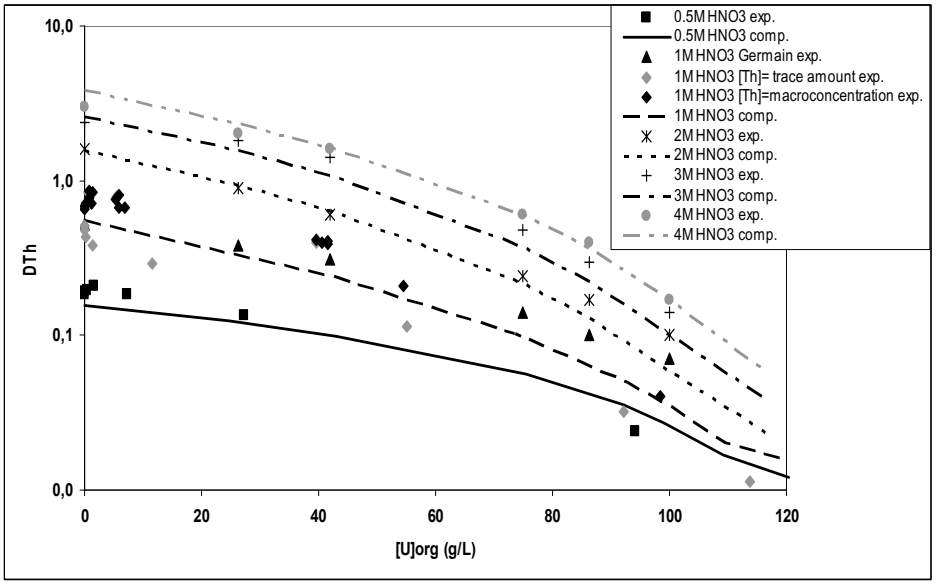

Fig.3. Comparison between computed and experimental Th(IV) distribution ratios used for the optimization of pseudo-constants for HNO3= 0.5, 1, 2, 3 and 4 M.

3.3. Confrontation with feed back from an uranium cycle (La Hague plant)

As mentioned previously, thorium build-up occurs in the extraction section of an uranium purification cycle, just behind the uranium front (cf. Fig 4). Before shutdown, the cycle is fed with treated uranium to eliminate remaining impurities present in the extractors, like thorium. Thorium concentration in an appropriate stage of the extractor (cf.Fig 4) was monitored during this procedure, giving evidence of the decrease of thorium build-up in the extractor during this procedure. The PAREX code was used to simulate the monitored thorium concentration, and as shown in figure 5, the computed results are in good agreement with experimental values.

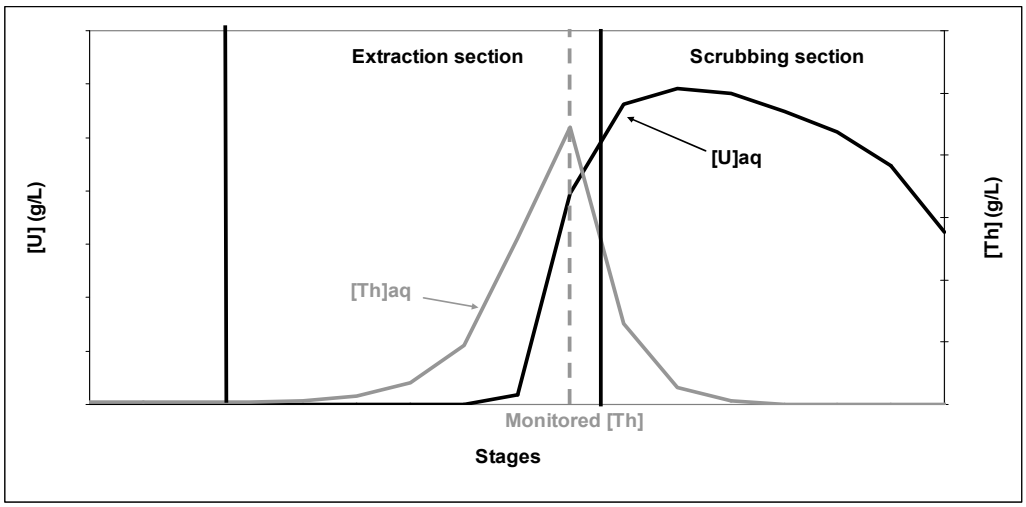

Fig.4. Accumulation of thorium, behind the uranium front, in extraction section of an uranium purification cycle (steady-state).

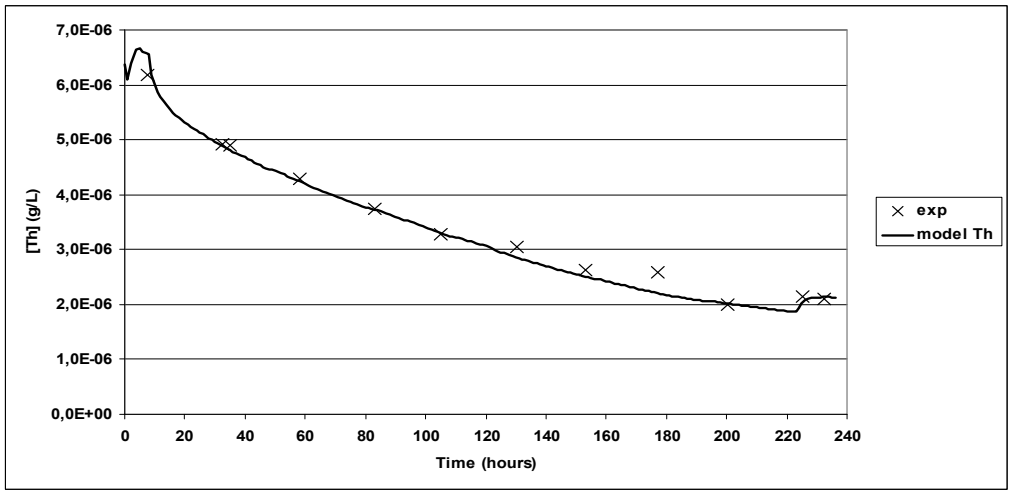

Fig.5. Comparison between computed and experimental behaviour of thorium during a shutdown procedure in the reprocessing plant.

3.4. Confrontation to other distribution data

The model was confronted with literature data obtained for other conditions than those used for the optimization: data without uranium published by S.Watson [2], R.Ewing [3], T.Nakashima [4] and in this work (cf. Fig. 6), and data coming from Nakashima publication [4] obtained for higher thorium concentration (cf. Fig. 7)

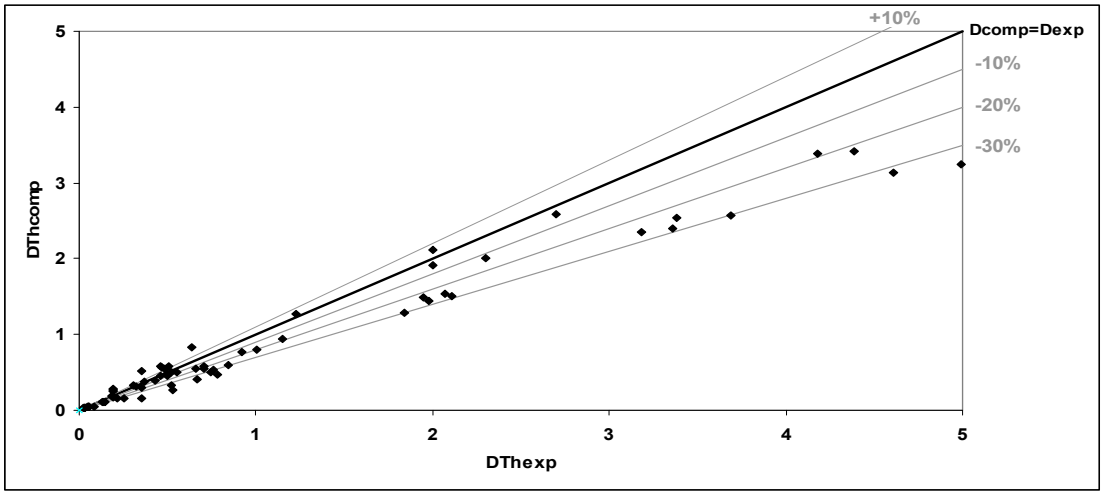

Fig.6. Comparison between computed and experimental Th(IV) distribution ratios obtained without uranium, 0.1 M ≤ [HNO3]aq ≤ 3.9 M, 0.72 ng/L ≤ [Th]aq ≤ 393 g/L.

As can be seen in figure 6, thorium computed extraction is underestimated for thorium high distribution ratios (RMS=24.7%, MD=-11.93%).

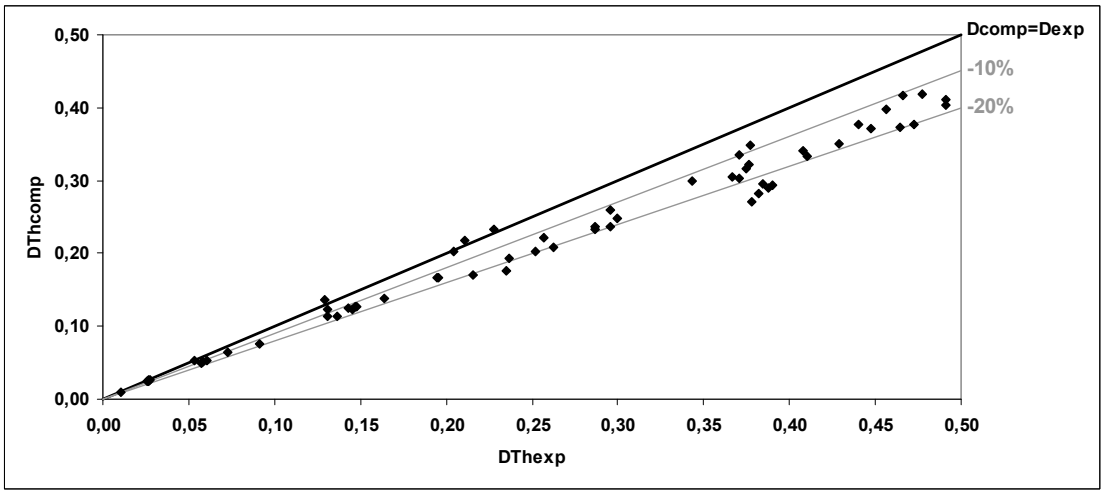

Fig.7. Comparison between computed and experimental Th(IV) distribution ratios obtained in presence of uranium (3 mg/L ≤ [U]aq ≤ 17 g/L) and high thorium concentrations (140 mg/L ≤ [Th]aq ≤ 93 g/L), 0.1 M ≤ [HNO3]aq ≤ 0.6 M.

According figure 7, the model remains valid (RMS=15.8%, MD=-14%) in a wide area of thorium concentration and uranium-thorium ratio concentration. In general way, thorium computed extraction is lightly underestimated for thorium high distribution ratios.

4. Conclusion

Using data published by Germain and additional measurements done in this work, we were able to build a model for thorium extraction by TBP. The implementation of this model in the PAREX code allowed a good simulation of thorium behaviour in an uranium purification cycle.

However this model is perfectible. More data will be needed to enhance its precision or to extend its validation domain.

Acknowledgements

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